



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 246 366
A1**

12

EUROPEAN PATENT APPLICATION

21 Application number: **86200903.2**

51 Int. Cl.4: **C11C 3/12**

22 Date of filing: **23.05.86**

43 Date of publication of application:
25.11.87 Bulletin 87/48

64 Designated Contracting States:
AT BE CH DE FR GB IT LI NL

71 Applicant: **THE PROCTER & GAMBLE
COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

72 Inventor: **White, Robert Lee**
8992 Cotillion Dr.
Cincinnati, OH 45231(US)
Inventor: **McGrady, Joseph**
1526 Lemontree Dr.
Cincinnati, OH 45240(US)

7A Representative: **Suslic, Lydia et al**
Procter & Gamble European Technical
Center N.V. Temselaan 100
B-1820 Strombeek-Bever(BE)

54 Hydrogenation process for making rapid melting fats.

57 A single-stage process for catalytically hydrogenating liquid oils is disclosed. In this process a liquid oil having an iodine value of from about 95 to about 145 is hydrogenated in the presence of a partially deactivated nickel catalyst having a concentration of nickel of from about 0.01% to about 0.2% by weight of the oil. The hydrogenation process is carried out at a temperature which is gradually increased from a starting temperature of from about 160°C (320°F) to about 200°C (392°F) to a final temperature of from about 210°C (410°F) to about 250°C (482°F) and a pressure of from about 0 psig to about 100 psig. The process is terminated when the iodine value of the oil reaches a value of from about 65 to about 91. This process produces a hydrogenated oil having a solids content index of not higher than about 6 at 33°C (92°F) and a solids content index of at least about 17 between 21°C (70°F) and 33°C (92°F).

EP 0 246 366 A1

HYDROGENATION PROCESS FOR MAKING RAPID MELTING FATS

Technical Field

The present invention relates to a process for hydrogenating a liquid oil to provide a product with a unique melt profile.

Background of the Invention

Textural characteristics, and particularly mouthmelt, of products containing hydrogenated oils, such as margarines, ice creams, frostings, cookies, and baked goods, depend to a great extent on the solids content index (SCI) of the hydrogenated oils. Margarine products, for example, should melt readily in the mouth to avoid a sensation of waxiness or stickiness. Baked products such as cookies and cakes should also have fats which melt readily in the mouth to avoid the sensation of graininess or toughness. On the other hand, the presence of some solid fat gives a slightly crispy or cake-like texture initially.

It has now been discovered that fats having an SCI of not higher than 6 at 33°C (92°F) and an SCI spread of at least 17 between 21°C (70°F) and 33°C (92°F), when processed into margarine or other products, result in a greatly enhanced mouthmelt, flavor display, and taste. These fats also make excellent baked goods products, particularly cookies. However, most hydrogenation processes known in the art produce fats having an SCI at 10°C (50°F) of from approximately 40 to 70, an SCI at 21°C (70°F) of from approximately 45 to approximately 65, and an SCI at 33°C (92°F) of from approximately 10 to approximately 30. Therefore, a new hydrogenation process had to be developed to efficiently produce a fat having the desired melt characteristics.

Primarily, hydrogenation is a means of converting liquid oils to semisolid, plastic fats suitable for shortening or margarine manufacture. However, it also accomplishes various other desirable purposes, including enhancement of the stability and the improvement of the color of the fat.

Hydrogenation is the addition of hydrogen to the double bonds (unsaturated or ethylenic bonds) of an oil or fat by reaction with hydrogen in the presence of a metal catalyst. It is a means of saturating oils. However, the hydrogenation reaction is complicated by the simultaneous isomerization, both positional and geometrical, of the unsaturated bonds. The position of the fatty acid on the glycerol as well as the degree of unsaturation determines the physical properties of the molecule, particularly the melting point of the fat or oil. In general, there is a stepwise conversion of the most unsaturated fatty acid form to the saturated state, i.e., linolenic to linoleic, then to oleic, and finally to stearic.

Conventional hydrogenation techniques normally do not yield products with a narrow melting range or controlled levels of trans acids (e.g., trans-isomers of octadecenoic acid). Trans acids are generally higher melting than the corresponding cis-isomer, although this may not always be the case, since melting point is also dependent upon the position of the double bonds. The trans fatty acid triglycerides contribute to increased levels of intermediate melting triglycerides in a hydrogenated oil. With conventional hydrogenation techniques an equilibrium is ultimately reached in the final stages in which the monounsaturated acids comprise approximately two-thirds trans-isomers and one-third cis-isomers. This level of trans acid content is not sufficient to permit the hydrogenated oil to have the melting range preferred herein.

U.S. Patent 4,169,843, Snyder, issued October 2, 1979, discloses a method for the hydrogenation of liquid oils, particularly vegetable oils, at a temperature of from 190°C (374°F) to 235°C (455°F) and a pressure of from about 103 to 1030 mm mercury. The product usually contains less than 10% stearate, less than 7% diene fatty acid glycerides, and greater than 60% trans-isomers of unsaturated fatty acid glycerides. The Snyder process uses a mixture of a conventional nickel catalyst and a sulfur-poisoned nickel catalyst. The SCI values of the hydrogenated fats are 57 to 67 at 10°C (50°F); 44 to 59 at 21°C (70°F); and 13 to 19 at 33°C (92°F).

U.S. Patent 3,459,777, Seiden, issued August 5, 1969, discloses a process for catalytically hydrogenating vegetable oils and margarine oils at a temperature of between 180°C (356°F) and 240°C (464°F) and a pressure between 0 psig and 100 psig. This process includes the steps of adding catalyst at the beginning of the reaction in an amount sufficient only to start the hydrogenation and subsequently incrementally adding catalyst at a minimum prescribed frequency designed to cause the reaction to follow a predeter-

mined refractive index/time curve. Example 1 discloses a batch process for partially hydrogenating Canbra oil to an SCI of 46.78 at 10°C (50°F), 23.0 at 21°C (70°F) and 0.0 at 33°C (92°F), and states that a conventional hydrogenated product would have an SCI of 39.8 at 50°F, 21.2 at 21°C (70°F), and 0.5 at 33°C (92°F).

- 5 U.S. Patent 3,856,831, Tateishi et al, issued Dec. 24, 1974, discloses a process for hydrogenating an oil having an initial IV between 60 and 78 utilizing a sulfur-poisoned nickel catalyst, preferably carried out at a temperature between about 160°C (320°F) and 220°C (428°F), which produces a fat with an SCI at 10°C (50°F) of approximately 40; at 21°C (70°F) of approximately 20; and at 33°C (92°F) of approximately 6.

- 10 U.S. Patent 4,134,905, Hassman, issued January 16, 1979, discloses a two-step hydrogenation process utilizing a copper chromate catalyst in the first step and a nickel catalyst in the second step, which produces a fat having an SCI at 10°C (50°F) of 62 to 64; at 70°F (21°C) of 49 to 53; and at 33°C (92°F) of 22 to 29.

- Both Swern, Bailey's Industrial Oil and Fat Products, 3rd ed., 1964, pp. 305-313 and 793-886, and Swern, Bailey's Industrial Oil and Fat Products Vol. 2, 4th ed., 1982, pp. 5-69, discuss the hydrogenation 15 process in general and of the use and theory of SCI measurements. Beckmann, "Hydrogenation Practice", JAOCS, Vol. 60, No. 2, February 1983, pp. 282-290, discusses hydrogenation theory and practice. Heat-saving equipment and process control are also discussed. These discussions track conventional catalyst, and single temperature and pressure process parameters.

- The process herein is a single-stage process. All the reactants are mixed and reacted in one step. This 20 can be distinguished from processes such as that of Hassman, which utilizes two separate hydrogenation steps using different catalysts, or processes such as that of Seiden, which utilizes multiple catalyst additions. The present process is considerably simpler, more efficient, and quicker than the multiple-step processes.

- It is an object of this invention to provide a hydrogenation process whereby a hydrogenated oil is 25 produced having SCI characteristics well adapted for use in edible products requiring quick melting or dissipation in the mouth but relative stability at room temperature. Preferably, this product is beta-prime stable.

- It is a further object of this invention to provide a simple, rapid, single-step process for producing the 30 above hydrogenated oils.

Summary of the Invention

- Hydrogenation of an oil having an initial iodine value (IV) of from about 95 to about 145 is carried out in 35 the presence of a partially deactivated nickel catalyst present at a concentration of from about 0.01% to about 0.2% nickel by weight of oil at a temperature which is increased gradually from a starting temperature of from about 160°C (320°F) to about 200°C (392°F) to a final temperature of from about 210°C (410°F) to about 250°C (482°F). The pressure exerted during the hydrogenation ranges from about 0 psig to about 100 psig. The reaction is terminated when the iodine value (IV) reaches a value of from about 65 to about 40 91. This produces a hydrogenated oil having an SCI of not higher than about 6 at 33°C (92°F) and an SCI spread of at least 17 between 21°C (70°F) and 33°C (92°F).

Detailed Description of the Invention

- 45 This invention relates to the hydrogenation of oils and more particularly to partial and selective hydrogenation of animal, marine and vegetable oils having fatty acid chains comprising 14 or more carbon atoms. The process provides hydrogenated oils having a specific solids content which gives sharper melting point ranges. The products have particular utility in the formulation of margarines, cookie products, 50 ice cream coating fats, hard butters, frostings, and in other similar applications in which quick melting and improved eating qualities of the product are required.

- For hydrogenation to take place, gaseous hydrogen, liquid oil, and the solid catalyst must be brought together at a suitable temperature. In ordinary practice it may be assumed that the hydrogen is first brought into contact with the oil, with the hydrogen-laden oil then brought into contact with the catalyst by 55 mechanical means. In the usual type of equipment, a suspension of catalyst and oil is agitated in a closed vessel in an atmosphere of hydrogen. Agitation of the catalyst-oil mixture promotes dissolution of hydrogen in the oil and continuously renews the oil at the catalyst surface. The solubility of hydrogen and other gases in oil increases linearly with temperature and pressure.

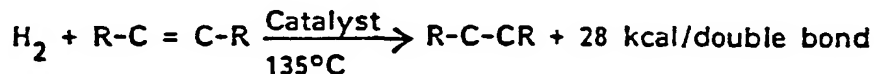
The rate of hydrogenation under the conditions just outlined depends on the temperature, the nature of the oil, the activity of the catalyst, the concentration of the catalyst, and the rate at which hydrogen and unsaturated oil are mixed at the active catalyst surface. The composition and the character of the hydrogenated product can vary according to the positions of the double bonds which are hydrogenated, as well as certain isomerizing influences accompanying the reaction, and are highly dependent on the conditions of hydrogenation.

Hydrogenation, like other chemical reactions, is accelerated by an increase in temperature or pressure. Also, as the temperature of reaction is increased, the formation of trans unsaturation increases almost linearly. The effect of pressure on isomerization is limited, and the rate of increase in the formation of trans isomers is less at higher pressures.

Commercial hydrogenation plants are essentially divided between "recirculation" systems, in which agitation and dispersion of hydrogen within the oil are achieved by continuously recycling hydrogen in large volumes through the reactor, and the newer "dead-end" systems in which the reactor is supplied only with as much hydrogen as is absorbed, and where dispersion of the hydrogen is assisted by mechanical agitation. For a thorough discussion of hydrogenation equipment, see Swern, Bailey's Industrial Oil and Fat Products, Vol 2, 4th ed., 1982, pp. 27-37.

For hydrogenation to occur, gaseous hydrogen, liquid oil, and a catalyst must be brought together at the necessary activation energy level. Thereafter, it is an exothermic reaction that produces more energy than needed to sustain the reactor system.

The chemical reaction follows:



When a double bond which has complexed with the metal catalyst loses activation energy and has not acquired a hydrogen atom, it desorbs from the catalyst. As electron density is returned to the C = C pi bond, the adjacent C-H sigma bond may rotate to the opposite side forming the trans-isomer.

As unsaturated fatty acids become saturated, their melting point increases. At equal saturation levels the melting point of the trans form is higher than the cis form. Thus, the mixture is really composed of liquids and solids. The analytical method which reflects or indicates a comparison percentage solid phase at a given temperature is the solids content index (SCI). This indicates the melting behavior of hydrogenated products and becomes a useful target for process control and product formulation.

The starting oil for the process of the present invention can be any liquid vegetable, animal or marine oil or blend of oils which is low in saturated fatty acids and has an iodine value of from about 95 to about 145. The preferred oil is a polyunsaturated vegetable oil having fatty acid chains containing at least 14 carbon atoms. Preferred vegetable oils include soybean, cottonseed, sunflowerseed, safflower, olive, peanut, coconut, palm, palm oil olein, and Canola oil. More preferred oils include soybean, sunflowerseed and corn oil. The most preferred oil is soybean oil. Preferred marine oils include menhaden, pilcherd, sardine and herring oil.

Usually, a blend of two or more oils is used to obtain the desired initial IV values and the desired beta-prime stability in the hydrogenated oil. The oils may be blended either prior to or following hydrogenation. Preferred blends contain soybean, sunflowerseed or corn oil, which contain many unsaturated fatty acids, both mono-unsaturated fatty acids and di-and tri-unsaturated fatty acids.

Oils with high iodine values, such as palm oil, are useful in limited amounts when blended with an oil low in saturated fatty acids, and therefore having a low iodine value, such as soybean oil.

Many preferred oil blends used in this process are beta-prime stable. By beta-prime stable is meant the oil eventually crystallizes into and remains predominantly in the crystalline form known as beta-prime. This is in contrast to oils which remain predominantly in the alpha crystalline form or quickly crystallize into the beta crystalline form. Oils which contribute to beta-prime stability are oils high in palmitic acid in the 1 and 3 position of the glycerol, such as cottonseed oil, palm oil, and palm oil olein.

The oil is mixed with a hydrogenation catalyst which is partially deactivated. The deactivated catalyst is necessary to control the reaction rate. Finely divided metallic nickel catalysts are well known for use in the hydrogenation of vegetable oils. Such catalysts are usually deposited on carriers such as Kieselguhr, aluminum oxide, silicate and the like.

Nickel catalysts lose their activity, or are deactivated, during the reaction due to the poisoning action of certain chemical substances, such as sulfur, phosphorus, chlorine, zinc, and compounds of the same, and more particularly due to the formation of soaps or fatty acid compounds of nickel. Use of a partially deactivated catalyst is necessary in the present process to control the rate of the reaction, and thereby the relative proportions of cis and trans fatty acid triglycerides in the products formed.

The preferred catalyst is a sulfur-poisoned deactivated nickel catalyst. Sulfur-poisoned nickel catalysts useful in the catalyst system of the present invention contain from about 5% to about 20% sulfur based on the nickel present in the sulfur-poisoned catalyst portion of the catalyst system. Commercially prepared catalysts are available. One method for preparing sulfur-poisoned catalyst is described in U.S. Patent No. 3,856,831 of Tateishi et al (Dec. 24, 1974). A conventional reduced nickel hydrogenation catalyst is subjected to an atmosphere containing hydrogen sulfide for sufficient time to obtain the desired sulfur content. Other methods for preparing a deactivated nickel catalyst include reducing a nickel compound, such as the oxides, hydroxides or carbonates, and then reacting the nickel catalyst with a mixed gas stream containing hydrogen and hydrogen sulfide until the desired sulfur content is obtained. Either wet-reduced nickel catalyst or dry-reduced nickel catalyst can be used.

A preferred method for preparing the sulfur-poisoned catalyst is to mix from about 5% to about 25% nickel catalyst into melted hardened coconut oil (IV less than 1). The mixture is then heated to a temperature in the range of from about 70°C (174°F) to about 90°C (194°F), elemental sulfur is added and the mass is quickly heated to a temperature of about 180°C (356°F) while being stirred in a nitrogen atmosphere. The liquid mass is maintained at a temperature of from about 180°C (356°F) to 210°C (410°F) for about 1 hour. Thereafter, the mass is cooled while being stirred to provide a uniform catalyst mixture.

The partially deactivated nickel catalyst used in the present invention is utilized at a concentration of from about 0.01% to about 0.2%, preferably from about 0.03% to about 0.1%, and most preferably from about 0.05% to about 0.08% by weight of nickel/weight of oil. The amount of catalyst used is dependent upon the rate of reaction to be attained and other variables such as temperature and pressure, and the starting oil. Certain oils, particularly mustard seed and Canola oils, contain organic sulfur compounds which act as catalyst poisons. The primary volatile sulfur compounds found in Canola oil include allyl isothiocyanate, 3-butenyl isothiocyanate, 4-pentenyl isothiocyanate, and 2-phenethyl isothiocyanate. When hydrogenating oils high in organic sulfur compounds, it may be necessary to use a large amount of a nickel catalyst containing a minimal amount of sulfur. Hydrogen impurities may also contribute to the deactivation of the catalyst. Thus, if hydrogen high in contaminants such as hydrogen sulfide and carbon monoxide is used, it may be necessary to compensate by decreasing the amount of sulfur in the catalyst or by increasing the amount of catalyst used. The catalyst may be recycled, and in fact catalyst which has been recycled a few times is preferred over fresh catalyst. Recycled catalyst is often combined with fresh catalyst to obtain the desired activity level.

Any type of commercially acceptable processing operation, including batch hydrogenation, continuous processing recirculation systems, and "dead-end" systems, may be utilized with the process described herein. The process described herein is a single-stage process. The hydrogen, oil, and catalyst are contacted or mixed in a single step, and the reaction then proceeds to completion.

The process is carried out for from about 30 minutes to about 8 hours, and preferably from about 1 hour to about 4 hours. The pressure ranges from about 0 psig to about 100 psig, and preferably from about 0 psig to about 40 psig. The pressure can remain constant throughout the hydrogenation process or can be changed during the reaction. It is often desirable to control the rate of reaction by manipulating the pressure in the reaction vessel. The pressure should be manipulated in such a way as to maintain a rate of reaction high enough to allow completion of the hydrogenation within a reasonable time period, but not so high as to significantly decrease the selectivity of the reaction. It may be desirable to decrease the pressure, thereby decreasing the rate of reaction, toward the end of the hydrogenation to allow adequate control of the termination point. Pressure is controlled by valves which release hydrogen from the reactor or add additional hydrogen to the reaction vessel.

The temperature of the reaction is gradually increased from a starting temperature of from about 160°C (320°F) to about 200°C (392°F), and preferably about 180°C (356°F), to a final temperature of from about 210°C (410°F) to about 250°C (482°F), and preferably about 240°C (464°F). The method used to control the temperature of the reactor varies with the processing equipment. Since hydrogenation is an exothermic reaction, it may be necessary to cool the reaction by some suitable means, such as a heat exchanger. However, if the vessel is not well insulated or is in a large unheated area, the system may lose heat quickly enough that the heat generated by the exothermic reaction will not be sufficient to maintain the reaction

temperature or to allow for the gradual rise required by the process herein. In this case, it is necessary to apply additional heat by some suitable means, such as heating coils or external heating means such as heating jacket or heat exchangers. Heat may be applied either continuously or periodically, depending on the requirements of the system.

- 5 The temperature increase of the process is preferably controlled by the gradual rise occurring through the exothermic reaction. However, in those cases where additional heat is required, the temperature increase is a gradual or a step-wise increase over the reaction period.

The reaction is terminated when the iodine value (IV) reaches a value of from about 65 to about 91, and preferably from about 70 to about 88. This is just before any significant amount (6%) of the mono-unsaturated fatty acid is converted to saturated. By terminating the reaction at this point, the percentage of octadecenoic acid is maximized, the percentage of octadecadienoic acid is minimized, and the level of stearic acid is minimized. The IV at which this point is reached depends upon the initial fatty acid content of the oil or blend of oils which are hydrogenated. It is very important to terminate hydrogenation at the proper point, since continuation beyond this point will result in a fat having undesirably high SCI values and a narrower SCI spread.

15 The fats produced have an SCI spread of at least about 17, and preferably at least 33, between 21°C (70°F) and 33°C (92°F) and an SCI of not higher than about 6, and preferably not higher than about 2, at 33°C (92°F).

When the fats made by the above process are utilized in products such as margarines, cookies, baked goods, and frostings, these products have characteristics at various temperatures which make them appealing to the consumer, convenient to use, easy to store, and resistant to deterioration. These physical characteristics are to a great extent dependent on the type of fatty material used in the product and more particularly on the percentages of the fatty matter which exist in the solid state at the various temperatures normally encountered during the storage, use and consumption of the product.

25 A conventional margarine product, for example, should melt readily in the mouth to avoid a sensation of waxiness or stickiness and to have a satisfactory flavor. This means there should be little or no fatty material in the solid state at or near mouth temperatures during mastication (about 32°C (90°F) to 35°C (95°F)). However, at temperatures of use (about 18°C (65°F) to 29°C (85°F)), it must be capable of being spread and this requires that some portion of the fatty material be in the solid state, but not so much that the margarine is hard and difficult to spread and not so little that the margarine will slump or lose its shape. In addition, the margarine should have good stability to permit storage of the product in the refrigerator or at room temperature.

The solid content referred to hereinabove is expressed at different temperatures, in terms of a "Solids Contents Index" (SCI) which is measured by what is essentially the test described in the Journal of the American Oil Chemists' Society, March 1954, Vol. XXXI, pp. 98-103. The test involves a dilatometric measurement of the amount by which a fat expands when heated from a specific temperature to complete melting. Since this expansion is due to both a volume increase when solids change to liquids without a temperature change and a volume increase due to thermal expansion without change in phase from solid to liquid, allowance is made for the thermal expansion so that the change in volume gives a measure of the amount of solid phase present at the temperature of measurement. The test has been modified so that readings are taken after 30 minutes at the temperature of measurement. SCI data for an oil are often presented in a graph form wherein the abscissa is Temperature and the ordinant is SCI.

45 The Iodine Value is the number of grams of iodine absorbed by 100 g. of oil from an iodine bromine mixture. The Iodine Value may be determined by titration or calculated from the fatty acid composition data of the sample. Approximate iodine values may be determined by measurement of the refractive index of the oil, since for each given oil a linear correlation between iodine value and refractive index can be determined. This method allows a relatively quick and easy determination of the proper endpoint of the hydrogenation. The larger the iodine value, the more unsaturated the fat.

50 The following examples illustrate the broad range of applicability of the present invention, without intending to be limiting thereof. It will be appreciated that other modifications of the present invention, within the ordinary skill of those in the art, can be undertaken without departing from the spirit and scope of this invention.

All percentages are by weight percent unless otherwise specified.

Example 1

To 393 lbs. of soybean oil was added 50 g. of fresh sulfur-deactivated nickel catalyst (20% Ni) and 485 g. of recycled sulfur-deactivated nickel catalyst. Hydrogen was added to the 450 lb. stainless steel reaction vessel at a pressure of approximately 175 psig. Mechanical agitation was applied. The hydrogenation was carried out at a pressure of 0 psig according to the following table:

Table 1

<u>Time from start of hydrogenation (min.)</u>	<u>Refractive index Butryo scale 60°C</u>	<u>Temperature °C (°F)</u>
0	52.0	180 (355)
33	51.8	183 (362)
55	50.8	191 (375)
80	48.9	196 (385)
100	47.6	218 (425)
120	46.2	228 (443)
140	44.2	228 (442)
160	43.5	228 (442)
178	43.1	242 (467)
188	42.9	291 (465)
202	42.8	240 (462)
216	42.6	238 (460)

The hydrogenated product had the following characteristics:

IV: 81.8
 SCl: 10°C (50°F) — 53.5
 21°C (70°F) 35.9
 27°C (80°F) 22.8
 33°C (92°F) 0.13

% trans-unsaturated fatty acid; 63.90

fatty acid content: myristic (C-14) 0.1%
 palmitic (C-16) 9.0%
 stearic (C-18) 4.1%
 octadecenoic (C-18:1) 74.0%
 octadecadienoic (C-18:2) 11.3%
 octadecatrienoic (C-18:3) 0.3%
 arachidic (C-20) 0.9%
 behenic (C-22) 0.3%

Example 2

To -410 lbs. of a 80% soybean/20% cottonseed oil blend was added 550 g. of recycled sulfur-deactivated nickel (20% Ni) catalyst. The hydrogenation was carried out in a single step as in Example 1 according to the following table:

Table 2

Time from start of hydrogenation (min.)	Refractive index Butryo scale 60°C	Pressure (psig)	Temp.	
			°C	(°F)
0	50.65	0	184	(364)
13	50.7	0	185	(365)
30	50.65	26	187	(368)
48	49.7	56	192	(377)
60	48.2	58	201	(394)
80	57.5	36	203	(397)
95	46.1	40	208	(407)
105	44.8	40	210	(410)
120	43.6	35	208	(407)
133	43.3	28	209	(408)

The hydrogenated product had the following characteristics:

IV: 87.3

SCI: 10°C (50°F) 42.6

21°C (70°F) 25.2

27°C (80°F) 13.9

33°C (92°F) 0

% trans-unsaturated fatty acid: 54.4

fatty acid content: myristic (C-14) 0.2%

palmitic (C-16) 12.3%

stearic (C-18) 3.9%

octadecenoic (C-18:1) 64.1%

octadecadienoic (C-18:2) 18.0%

octadecatrienoic (C-18:3) 0.4%

arachidic (C-20) 0.7%

Example 3

To 420 lbs. of cottonseed oil was added 450 g. of fresh sulfur-deactivated nickel (20% Ni) catalyst. The hydrogenation was carried out in a single step, as in Example 1 according to the following table:

5

Table 3

	Time from start of hydrogenation (Min.)	Refractive index Butyro scale 60°C	Temperature °C (°F)
	0	48.2	177 (350)
10	18	48.2	177 (350)
	36	48.2	191 (375)
	60	48.2	199 (390)
	85	48.2	201 (393)
	103	47.7	199 (390)
20	130	47.0	297 (387)
	160	46.1	213 (415)
	190	44.7	214 (417)
	210	44.0	214 (417)
25	220	43.7	219 (427)
	236	42.8	221 (430)

The hydrogenated product had the following characteristics:

30	IV:	79.1	
	SCI:	10°C (50°F)	39.1
35		21°C (70°F)	25.2
		27°C (80°F)	17.1
		33°C (92°F)	3.8
40	% <u>trans</u> -unsaturated fatty acid:	41.3%	
	fatty acid content:	myristic (C-14)	0.6%
		palmitic (C-16)	22.8%
		stearic (C-18)	2.5%
45		octadecenoic (C-18:1)	52.4%
		octadecadienoic (C-18:2)	8.5%
		octadecatrienoic (C-18:3)	1.3%
50		arachidic (C-20)	0.4%

Claims

55

1. A single-stage process for catalytically hydrogenating liquid oils which comprises reacting a liquid oil having an iodine value of from about 95 to about 145 with hydrogen in the presence of a partially deactivated nickel catalyst wherein the nickel comprises from about 0.01% to about 0.2% by weight of oil at

a pressure of from about 0 psig to about 100 psig and at a temperature range wherein the temperature increases from a starting temperature of from about 160°C (320°F) to about 200°C (392°F), to a final temperature of from about 210°C (410°F) to about 250°C (482°F), until the iodine value of the liquid oil is from about 65 to about 91.

- 5 2. A process according to Claim 1 wherein the temperature of the reaction is gradually increased from a starting temperature of about 180°C (356°F) to a final temperature of about 240°C (464°F).
3. A process according to Claim 1 wherein the pressure of the reaction ranges from about 0 psig to about 40 psig.
4. A process according to Claim 1 wherein the reaction is terminated when the iodine value reaches a
10 value of from about 70 to about 88.
5. A process according to Claim 1 wherein the reaction is terminated at a time of from about 30 minutes to about 8 hours after initiation.
6. A process according to Claim 5 wherein the reaction is terminated at a time of from about 1 hour to about 4 hours after initiation.
- 15 7. A process according to Claim 4 wherein the reaction temperature is raised from a starting temperature of about 180°C (356°F) to a final temperature of from about 240°C (464°F) and the pressure of the reaction ranges from about 0 psig to about 40 psig.
8. A process according to Claim 1 wherein the partially deactivated nickel catalyst is present at a nickel concentration of from about 0.03% to about 0.1% by weight of oil.
- 20 9. A process according to Claim 1 wherein the partially deactivated nickel catalyst is a sulfur-poisoned nickel catalyst.
10. A process according to Claim 8 wherein the partially deactivated nickel catalyst is a sulfur-poisoned nickel catalyst.
11. A process according to Claim 9 wherein the sulfur-poisoned nickel catalyst is present at a
25 concentration of from about 0.05% to about 0.08% of nickel by weight of oil.
12. A process according to Claim 1, wherein the oil to be hydrogenated is a vegetable oil or blend of oils having fatty acid chains containing at least 14 carbon atoms.
13. A process according to Claim 12 wherein the oil or blend of oils to be hydrogenated is selected from the group consisting of soybean oil, sunflowerseed oil, safflower oil, corn oil, cottonseed oil, olive oil,
30 peanut oil, coconut oil, palm oil, palm oil olein, and Canola oil, and mixtures thereof.
14. A process according to Claim 13 wherein the oil to be hydrogenated is selected from the group consisting of soybean oil, sunflowerseed oil, and corn oil, and mixtures thereof.
15. A process according to Claim 13, wherein the oil to be hydrogenated is a blend of oils containing an oil selected from the group consisting of soybean oil, sunflowerseed oil, and corn oil.
- 35 16. A process according to Claim 14 wherein the oil to be hydrogenated is soybean oil.
17. A process according to Claim 12 wherein the oil to be hydrogenated is a blend of oils containing an oil selected from the group consisting of cottonseed oil, palm oil, and palm oil olein.
18. A process according to Claim 15 wherein the oil to be hydrogenated is a blend of oils containing an oil selected from the group consisting of cottonseed oil, palm oil, and palm oil olein.
- 40 19. A process according to Claim 18 wherein the oil to be hydrogenated is a blend of soybean oil and cottonseed oil.
20. A hydrogenated oil produced by the process of Claim 1 having an SCI of not higher than about 6 at 33°C (92°F) and an SCI spread of at least about 17 between 21°C (70°F) and 33°C (92°F).
21. A hydrogenated oil produced by the process of Claim 9 having an SCI of not higher than about 6 at
45 33°C (92°F) and an SCI spread of at least about 17 between 21°C (70°F) and 33°C (92°F).
22. A hydrogenated oil according to Claim 20 having an SCI of not higher than about 2 at 33°C (92°F).
23. A hydrogenated oil according to Claim 20 having an SCI spread of at least about 33 between 21°C (70°F) and 33°C (92°F).

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application number

EP 86 20 0903

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	GB-A-1 151 677 (PROCTER & GAMBLE) * Claims 1,2,6; page 3, lines 121-130; page 4, lines 26-35,47-61; examples I,III,V,VI * & US-A-3 459 777 (Cat. D)	1-7,12 -16,20 ,22,23	C 11 C 3/12
X	FR-A-1 429 975 (UNILEVER) * Claim A; page 1, column 1, paragraph 1; page 1, column 2; examples 1-3 * -----	1,3-6, 8-14, 16	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 11 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26-01-1987	Examiner PEETERS J.C.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			